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The peculiarities of anion vacancy distribution and the relationship between their concentration and the Tld-500 detector Tl output

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Abstract. A procedure has been developed for estimating the uniformity of anion vacancy distribution in TLD-500 detectors on the basis of anion-deficient corundum single crystals. Vacancy distribution topograms were constructed for TLD-500 detectors with different sensitivities to irradiation. Analysis of the topograms provided correlations between average anion vacancy concentrations and thermoluminescent (TL) yields in the main peak with a maximum at 450 K. To confirm the pattern of regularities, the effects of high-temperature annealing of TLD-500 samples in air at T=1700 K were studied depending on its duration. Increasing the annealing time from 40 to 105 minutes was found to correlatedly reduce the anion vacancy concentrations and TL-yields in the basic and high-temperature peaks at 450 and 830 K, respectively.

1. Introduction

The available data [1] indicate that the luminescent activity of anion-deficient corundum (α-$Al_2O_{3-\delta}$) crystals and TLD-500 detectors on their basis is associated with the presence of anion vacancies. However, no unambiguous correlation has been established as yet between anion vacancy concentration C_a and thermoluminscence (TL) yield in the main and high-temperature peaks at 450 and 830 K. Thus, it was shown in [2] that in samples with about equal C_a the TL-yields differed not only in the main (~2 times) but also the high-temperature peak (~3 times).

The value of C_a is usually determined as the sum of F- and F^+-center concentrations calculated from corresponding optical absorption (OA) coefficients by Smakula's forumla. For determining C_a, OA spectra are commonly measured several times near the TLD-500 detector's center since its size (∅5 mm) is close to that of the optical beams produced by formerly used spectrophotometers such as Specord UV-VIS, Beckman UV-5270, or Specord M40. Then the values of OA coefficients in the F^+- and F-center OA bands are averaged to compute the averaged local C_a (^LC_a). The thus determined values of ^LC_a lie in TLD-500 detectors in the range of $5\cdot10^{16}$ to $2\cdot10^{17}$ cm^{-3}. However, this approach does not allow for the non-uniformity of anion vacancy distribution in TLD-500 detectors and α-$Al_2O_{3-\delta}$ crystals which, as noted in various publications on crystal corundum growth [3], may occur, particularly where directional crystallization is employed.

The goal of this study, therefore, was to develop a technique for investigating non-uniformities in the distribution of anion vacancies, measuring topograms of the $C_a=f(x,y)$ type, calculating the bulk-averaged value of C_a (^AC_a), and finding possible correlations between the TL-yield and ^AC_a.

2. Samples and experimental techniques

The objects of this study were samples of TLD-500 detectors on the basis of α-$Al_2O_{3-\delta}$ single crystals. X-ray irradiation of the samples was performed using an URS-55 X-ray unit (Cu-anode, U_H=55 kV, I_{max}=18 mA). The TL curves were measured on a special automated installation at a rate of β=2 K/s in a range of T=300-1000 K. The TL signal was recorded by a FEU-142 photomultiplier (Gran Company, Russia) at a reduced sensitivity to the thermal radiation of the heater, whose maximal temperature could reach 1200 K.

OA and photoluminescence (PL) spectra were measured in the samples by Cary 60 and Cary Eclipse spectrophotometers, respectively. The concentrations of F and F^+ centers (C_F and C_{F+}, respectively) were determined from OA in the $h\nu_{m1}$=6.1 eV and $h\nu_{m2}$=4.8 eV bands, respectively, using Smakula's formula. According to [4], the oscillator strength was taken to be equal to 1.3 for the F center and to 0.65 for the F^+ center.

3. Results and discussion

For estimating the non-uniformity of anion vacancy distribution in the ∅5×1 mm^3 samples studied, which are used as TLD-500 detectors as well, OA spectra were measured locally at 9 points. The cross-section of the optical beam produced by the Cary 60 spectrophotometer used presented a 1x1 mm^2 square. It is important to note that such a problem was set up for α-$Al_2O_{3-\delta}$-based TLD-500 detectors for the first time. An essentially similar problem was addressed in [5] with the aim of developing a technique for growing round rods from α-$Al_2O_{3-\delta}$ for making TLD-500 detectors. However, that study investigated the distribution of defects along the rod to ensure that parts of the rod containing either minimum anion vacancies or maximum growth macrodefects are removed before detectors are made from it.

For illustration, figure 1 shows $C_a=f(x,y)$ 2D-dependency topograms for four TLD-500 samples with a conventionally low (a), medium (b, c), and high (d) TL-yield in the peak at 450 K (S_{450}). As can be seen from figure 1, the distribution of anion vacancies in the samples and, consequently, in the TLD-500 was not uniform.

For characterizing the non-uniformities we determined a maximum ($^{max}C_a$), minimum ($^{min}C_a$) and average (^AC_a) concentration of anion vacancies and rms deviation σ for each of the samples. The results are summarized in table 1. The latter and figure 1 show that in the sample under consideration the anion vacancies are most uniformly distributed across the bulk of sample No. 2 with the average TL-yield in the main peak (S_{450}=447 a.u.). It is characterized by the least change in C_a ($[^{max}C_a-^{min}C_a]$=min) and minimal $\sigma=1.1\cdot10^{16}$ cm^{-3}. In the other three samples, the values of $[^{max}C_a-^{min}C_a]$ and σ are almost 1.5–2 times greater.

The above results are therefore rather important, including from the practical standpoint. If anion vacancy concentrations are determined at random points in samples (^RC_a), which is often the case in such studies, it is unlikely that a clear correlation may be established between S_{450} and ^RC_a (figure 2, curves 1′ and 1″). If such a dependence on ^AC_a is represented as $S_{450}=f(^AC_a)$, a nearly linear relationship is revealed between S_{450} and ^AC_a with a correlation coefficient of 0.995 (figure 2, curve 2). This result is new and practically important for sorting TLD-500K detectors. On the other hand, the usage of samples with considerable σ should be restricted in annealing experiments where dependence on C_a is investigated and where small shifts of the measurement points are possible. This requirement of anion vacancy distribution uniformity in samples may be relaxed to some extent. It is important to ensure that the gradient of C_a be minimal in the region commensurate with the spectrophotometer's beam size and where its slight shifting is possible.

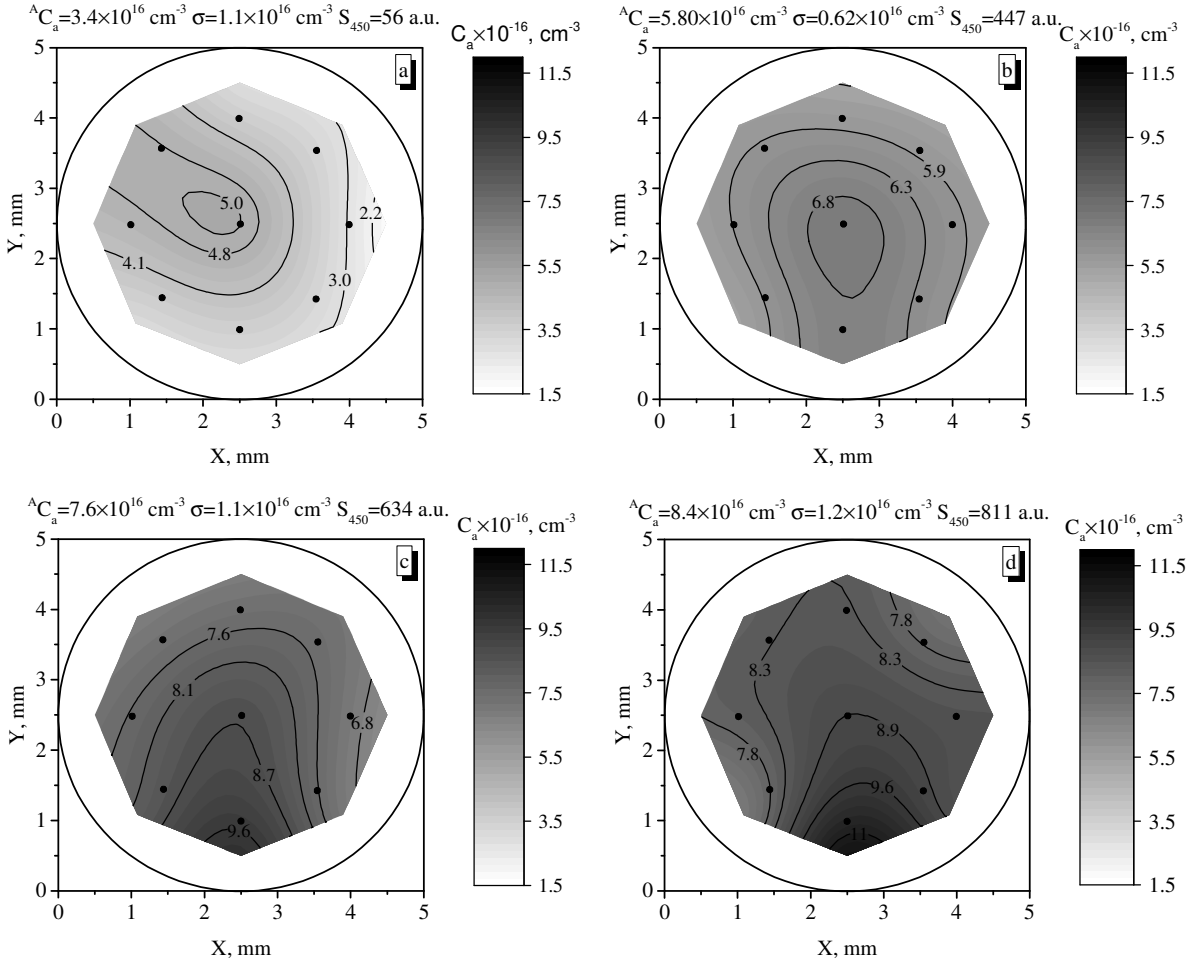

Figure 1. Topograms for the distribution of anion vacancies in four TLD-500 samples, respectively, with a low (a), medium (b, c) and high (d) TL-yield in the 450 K peak.

Table 1. Estimates of the parameters characterizing the bulk distribution of anion vacancies in the sample.

Sample number	S_{450} (a.u.)	$^{R}C_a$ (10^{16} cm^{-3})	$^{A}C_a$ (10^{16} cm^{-3})	$^{max}C_a$ (10^{16} cm^{-3})	$^{min}C_a$ (10^{16} cm^{-3})	σ (10^{16} cm^{-3})
1	56	2.5	3.4	5.0	1.8	1.1
2	447	7.0	5.8	7.1	5.2	0.6
3	634	6.5	7.6	9.9	6.3	1.1
4	811	11.0	8.4	11.2	7.0	1.2

Thus, the correlation dependence between TL-yield and C_a should be established allowing for any non-uniformity in the distribution of anion vacancies and their maximal, minimal and average values. Moreover, it follows from the above data analysis that for ensuring the reproducibility of active center concentration measurement results by the absorption method it is essential to minimize the number of resets (shifts) of samples in the course of the experiment.

To obtain additional data on the role of anion vacancies in the TL properties of α-$Al_2O_{3-δ}$ crystals and TLD-500 detectors on their basis in the 300-1000 K range, we also studied α-$Al_2O_{3-δ}$ crystals

annealed in air at T=1700 K. According to [6], these annealing conditions may restore the stoichiometric composition, i.e. $\delta \rightarrow 0$ with α-$Al_2O_{3-\delta}$ turning into α-Al_2O_3. We therefore then studied in more detail and systematically changes in ${}^{A}C_a$ and TL-yields in the above peaks depending on the duration of annealing in air at T=1700 K in several TLD-500 samples with a TL-peak at 830 K and C_a=(0.4÷1.0)·10^{17} cm^{-3}.

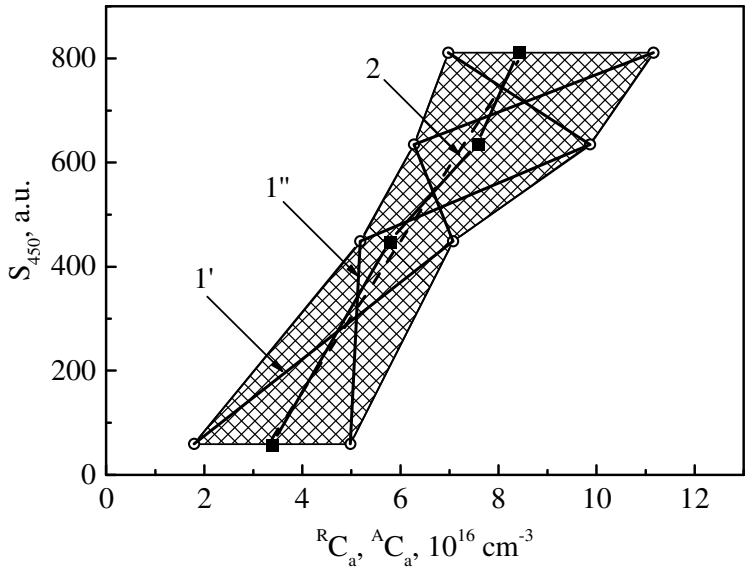

Figure 2. TL yields in the 450 K peak as a function of anion vacancy concentrations estimated at arbitrary points (1′ and 1″) in the samples and bulk averaged (2).

The typical changes in the absorption spectra of one of the TLD-500 samples subjected to oxidative thermal treatment depending on treatment time (t_a) are presented in figure 3. It shows that the concentration of F-centers and, hence, ${}^{A}C_a$ decreases as the annealing time increases. The anion deficiency disappeared in all samples studied after their thermal treatment at T=1700 K for 105 minutes. This is a novel result.

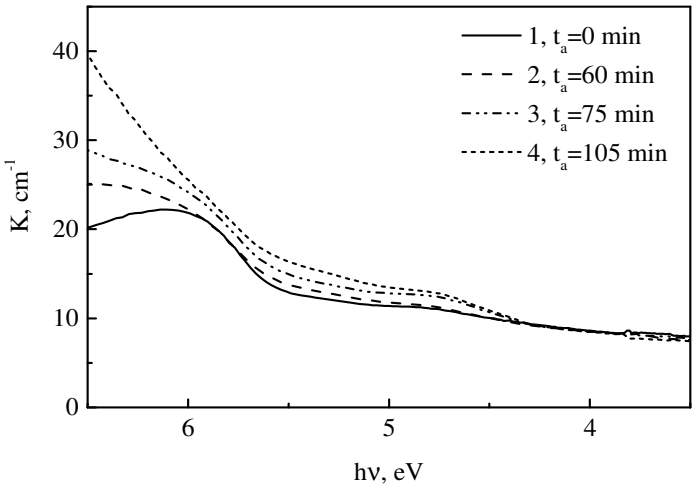

Figure 3. OA spectra of an α-$Al_2O_{3-\delta}$ samples with a TL-peak at 830 K before (1) and after high-temperature annealing in air at 1700 K for 60 min (2), 75 min (3) and 105 min (4).

A generalized picture of changes in ${}^{A}C_a$ and TL-yields in individual peaks depending on annealing time t_a in air at T=1700 K is shown in Figure 4. It demonstrates that even brief annealing for 10–20 minutes can meaningfully reduce TL-yields in the main and high-temperature peaks at 450, 515, 580 and 830 K, respectively (curves 1-4). Simultaneously emerges and grows a low-temperature peak at 410 K (curve 5) which, according to [7], is of a hole nature. This fact is in good agreement with the known consequences of oxidative thermal treatment [8], namely the development of hole color centers in oxides.

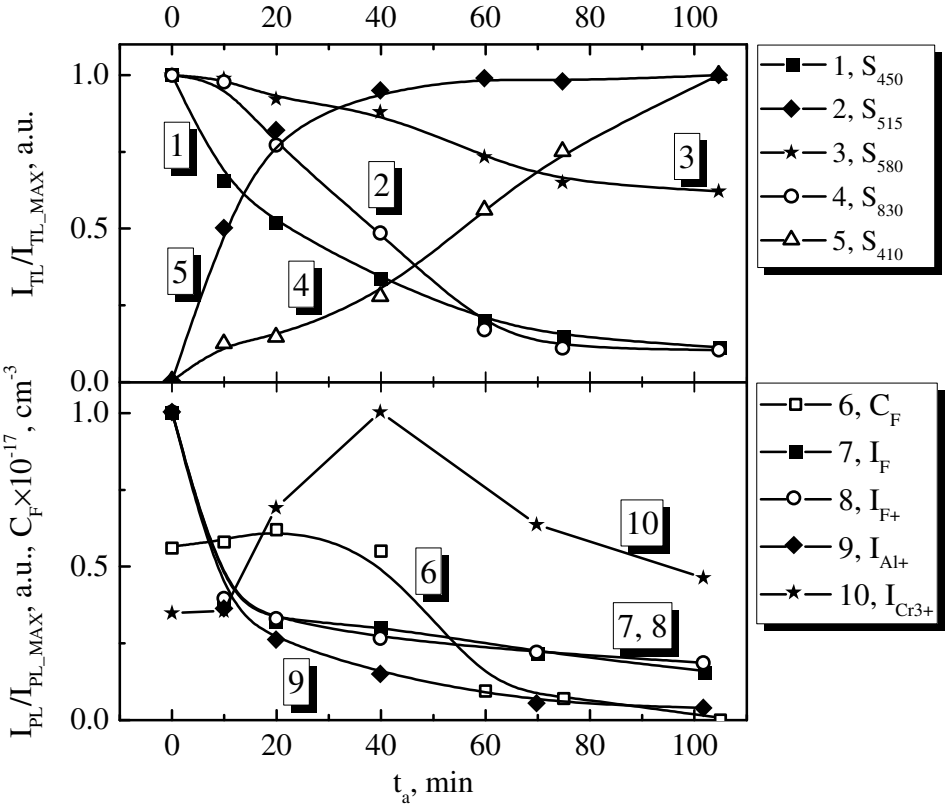

Figure 4. Normalized dependencies of TL-peaks in the peaks at 450 K (1), 515 K (2), 580 K (3), 830 K (4) and 410 K (5) on annealing duration at 1700 K in an α-$Al_2O_{3-\delta}$ sample with an 830 K peak irradiated with electrons at E_e=150 keV and D_e=20 kGy, and changes in the concentration of F-centers (6) and PL F-, F^+-, Al_i^+- and Cr^{3+}-centers at $h\nu_{em}$=3.0 eV and $h\nu_{ex}$=5.9 eV, $h\nu_{em}$=3.8 eV and $h\nu_{ex}$=4.8 eV, $h\nu_{em}$=2.4 eV and $h\nu_{ex}$=4.1 eV, and $h\nu_{em}$=1.8 eV and $h\nu_{ex}$=2.2 eV, respectively.

These tendencies of change in the TL-yield at 410, 450, 580 and 830 K persist up until t_a=105 minutes. However, whereas the 450 and 830 K peaks decreased by more than 10 times, the chromium peak did by only ~1.5 times. Moreover, after a 10-min annealing, a TL-peaks emerges at 515 K, which grows till t_a=40 min. (curve 2). Further on at t_a>40 min, the TL-yield at 515 K becomes saturated. According to [9], the nature of the 515 K peak may be associated with Al_i^+- or Ti_i^+-centers. It is important that the Ti_i^+-center has a similar structure to the Al_i^+-center, but the former has in its octahedral interstitial site a titanium ion impurity. Then the decrease in the PL of Al_i^+-centers at annealing and simultaneous growth in the TL-yield in the peak at 515 K (figure 4, curves 9 and 2, respectively) may provide evidence of a relationship of the 515 K peak precisely with Ti_i^+-centers. One of the arguments in favor of this hypothesis is the fact that stepwise annealing results in the concentration of Al_i^+-centers and their PL changing almost synchronously [2].

Worthy of special attention is the change in the anion vacancy concentration (${}^{A}C_a$) at annealing (figure 4, curve 6). At short annealing times ($t_a \leq 40$ min.) it even increased insignificantly (1.1 times). Then at $t_a \geq 40$ min it is observed to fall off sharply, and at $t_a = 105$ min the value of ${}^{A}C_a$ goes down to an OA-spectrally undetectable level. However, the PL data (see figure 4, curve 7) point to a non-zero concentration of F-centers and, consequently, anion vacancies in the sample annealed for $t_a = 105$ min at $T = 1700$ K. In the same way as the PL of F-centers can change under annealing, so can the PL-response of F^+- and Al_i^+-centers (see figure 4, curves 8 and 9). The drop in the PL-yield of Al_i^+-centers with an increase in t_a with a simultaneous decrease in ${}^{A}C_a$, the PL of F^+- and F-centers provides additional evidence that they have oxygen vacancies along with interstitial aluminium.

Unlike the PL-yields of F^+-, F- and Al_i^+-centers, as t_a is increased to 105 min, the PL of impurity Cr^{3+}-ions goes through a maximum at $t_a = 40$ min and smoothly decreases to the level observed at the beginning of annealing (figure 4, curve 10). The growth in the PL of Cr^{3+}-centers at $0 \leq t_a \leq 40$ min may point to the release of Cr^{3+} ions from a compound defect complex causing a high TL-activity of α-$Al_2O_{3-\delta}$ and containing anion vacancies along with Cr^{3+}-ions. The further decrease in the PL of Cr^{3+}-centers at $t_a \geq 40$ min is likely to be caused by their conversion into Cr^{4+}-centers as a result of their oxidation.

4. Conclusion

A spectrophotometric technique has been developed for estimating the uniformity of anion vacancy distribution in TLD-500 detectors and flat single crystal α-$Al_2O_{3-\delta}$ samples dia. 5 mm and over. The technique involves local measurement of optical absorption in the F^+- and F-center bands, determination of their overall concentration at a measurement point (local region), and construction of 2D-diagrams. We have found that such distribution may be considerably uneven in α-$Al_2O_{3-\delta}$ and TLD-500 samples studied. Based on this result, we have shown for the first time that the TL-yield in the main peak at 450 K in α-$Al_2O_{3-\delta}$ samples and TLD-500 detectors on their basis correlates with the average concentration of anion vacancies if determined by averaging the total concentrations of F^+- and F-centers measured locally at several points.

High temperature annealing of α-$Al_2O_{3-\delta}$ and TLD-500 samples in air at $T = 1700$ K, found to reduce the anion deficit, has demonstrated that there is a certain relationship between the concentration of anion vacancies and TL-yield not only in the main but also high-temperature peak at 830 K.

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